



Faculty of Resource Science and Technology

UTILIZING HETEROGENEOUS CATALYSTS FOR BIOFUEL PRODUCTION FROM PALM OIL WASTES

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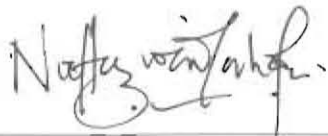
This project is submitted in partial fulfilment of the requirement for the Degree of
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DECLARATION

I hereby declare that no portion of the work referred to this final year project thesis has been submitted in support of an application for another degree of qualification to this or any other university or institution of higher learning.



(NURHAZWANI BINTI MOHAMED YAHAYA)

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ABSTRACT

An increase demand of biodiesel production triggered the researcher to look for low cost production of biodiesel. In this research, palm oil mill effluent (POME) wastes were used as feedstocks. The wastes were obtained from the cooling pond of POME from Kampung Endap, Samarahan. Transesterification reaction in the presence of methanol and catalyst was used to obtain the biodiesel. Two types of catalysts were used which heterogeneous catalyst and modified base catalyst. The used of modified base catalysts made the biodiesel existed in semi-solid form and difficult to be purified. However, the used of heterogeneous catalysts produced biodiesel in liquid form. The biodiesel was analysed using Fourier Transform Infrared (FTIR) Spectrometer.

Keywords: *heterogeneous, biodiesel, transesterification*

ABSTRAK

Permintaan pengeluaran biodiesel yang meningkat mencetuskan penyelidik untuk mencari kos pengeluaran biodiesel yang rendah. Sisa buangan kilang kelapa sawit digunakan dalam projek ini. Sisa tersebut didapati daripada kolam penyejukan di Kampung Endap, Samarahan. Transesterifikasi dengan kehadiran metanol dan katalis digunakan untuk menghasilkan biodiesel. Dua jenis katalis yang digunakan adalah heterogen dan pengubahsuaian bes katalis. Penggunaan bes katalis membuatkan biodiesel terhasil dalam bentuk separa solid dan sukar untuk ditulenkan. Walaubagaimanapun, penggunaan heterogen katalis telah menghasilkan biodiesel dalam bentuk cecair dan mudah untuk ditulenkan. Biodiesel dianalisis menggunakan spectrometer Fourier Transform Infrared (FTIR).

Kata Kunci: *heterogen, biodiesel, transesterifikasi*

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Scheme 1: Reaction for transesterification

LIST OF ABBREVIATIONS

POME	Palm Oil Mill Effluent
POMS	Palm Oil Mill Sludge
CaO	Calcium Oxide
NaOH	Sodium Hydroxide
FTIR	Fourier Transform Infrared
MgO	Magnesium Oxide
SrO	Strontium Oxide
BaO	Barium Oxide
HCl	Hydrochloric Acid

CHAPTER 1

INTRODUCTION

1.1 Background of Study

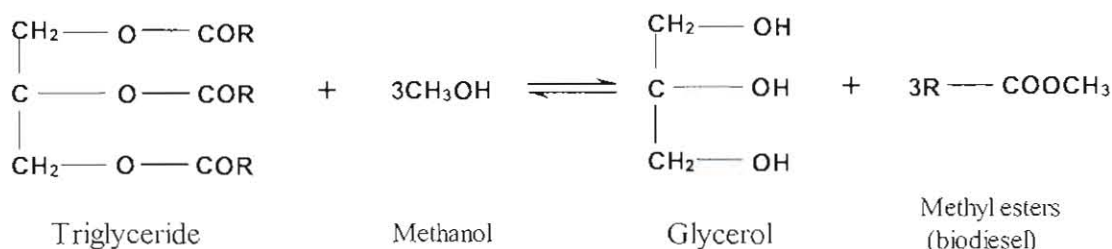
An increase demand of petroleum diesel has triggered researchers to find an alternative to produce energy from low carbon sources and eco-friendly technology. Biodiesel has gained international attention as a source of alternative fuel due to its high degradability, no toxicity, low emission of carbon monoxide, particular matter and unburned hydrocarbon (Al Zuhair, 2007; Vicente *et al.*, 1998).

Biodiesel is a liquid fuel which is similar to petroleum diesel in terms of combustion properties. It also has similar chemical and physical properties with petroleum diesel. However, biodiesel properties can sometimes be superior than that of petroleum diesel because the former has higher flash point, ultra-low sulphur concentration, better lubricating efficiency, and better cetane number (Chopade *et al.*, 2011), making it a cleaner burning fuel than petroleum diesel.

Palm oil is derived from the fleshy mesocarp of the fruit of oil palm. The oil palm industry has been recognised for its contribution towards economic growth and rapid development. It has also contributed to environmental pollution due to the production of high quantities of by-products from the oil extraction process (Rupani *et al.*, 2010). Currently, edible vegetable oils, such as palm oil, soybean, rapeseed and sunflower are the prevalent feedstocks for biodiesel production (Antolin *et al.*, 2002).

Large production of palm oil mill effluent (POME) can contribute to the water pollution. Vijayaraghayan *et al.* (2007) reported that during the period between 1990 and 2002, palm oil production was nearly doubled from 6,094,622 to 11,880,000 (MT) per year, making Malaysia the biggest palm oil producer worldwide. The rapid development of the industry has had serious consequences on the natural environment, which mainly related to water pollution. Discharging the POME on the land results in clogging and water logging of the soil and kills the vegetation on contact (Rupani *et al.*, 2010).

The production of biodiesel is performed by transesterification reaction of triglyceride with alcohol in the presence of catalyst (Demirbas, 2002). The reaction is shown in Figure 1. Many types of alcohol can be used such as methanol, ethanol, propanol, and butanol. The most common used is methanol because it gives a proper viscosity and boiling point and a high cetane number (Chantara-arpornchai *et al.*, 2012).



with R = mixture of various fatty acid chain.

Scheme 1: Reaction for transesterification.

Biodiesel is usually prepared in the presence of homogeneous or heterogeneous catalysts. During homogeneous catalytic transesterification, glycerol produced is low quality and requires lengthy process and distillation for purification. The removal of these catalysts is very difficult. Huge amount of water is needed in order to neutralize the

catalysts and causing a large amount of wastewater is produced during separating and cleaning the catalyst and the products. All these processing increase the costs of the end products; biodiesel and glycerol. The most common used are sodium hydroxide, sodium methoxide and potassium hydroxide.

The use of heterogeneous catalytic transesterification process has overcomes these problems as the methanol or ethanol does not mix with solid heterogeneous catalysts. After the transesterification reaction, it is relatively easy to separate the catalysts from biodiesel and glycerol (Chouhan and Sarma, 2011). The most common heterogeneous catalysts are calcium oxide (CaO) and magnesium oxide (MgO). Another catalyst used in transesterification which is a modified sodium hydroxide (NaOH) base catalysts. This catalyst is made from natural resource.

1.2 Problem Statement

The mass productions of POME have had serious consequences on the natural environment, which mainly relates to the water pollution. This is due to a large discharge of untreated or partially treated POME into watercourses. Therefore, to reduce the discharge into the watercourses, POME can be used as a feedstock in the production of biodiesel. The used of heterogeneous catalysts is one of the way to yield a high quality of biodiesel without producing a high amount of side products with a low cost process and in a short time.

1.3 Objectives

- a) To prepare heterogeneous catalyst from natural resources.
- b) To produce biodiesel from palm oil mill effluent (POME) and palm oil mill sludge (POMS).
- c) To compare the catalysts reactivity between CaO and modified NaOH Base.
- d) To characterize biodiesel by using Fourier Transformation Infra-Red (FTIR) spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction requires a catalyst, where is usually a strong base, such as sodium or potassium hydroxide to produces new chemical compounds called methyl esters. This esters is also known as biodiesel (Gcrpen, 2005). Chemically, biodiesel is defined as mono alkyl esters of long-chain fatty acids derived from renewable biolipids. It is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield methyl or methyl esters (biodiesel) and glycerine (Demirbas, 2002). Generally, methanol is preferred for transesterification because it is less expensive than ethanol (Graboski and McCormick, 1998).

In general, biodiesel may be defined as a domestic and renewable fuel for diesel engines derived from vegetable oil. Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of petrodiesel is non-explosive, with a flash point of 423K for biodiesel as compared to 337K for petrodiesel. Unlike petrodiesel, biodiesel is biodegradable and non-toxic and it significantly reduces toxic and other emissions when burned as a fuel. The production of biodiesel is more expensive compare to than petrodiesel, which therefore become a reason of less consumption of biodiesel itself.

2.2 Palm oil industry in Malaysia

Palm oil industry is one of the major contributors in Malaysia's economy. Malaysia and Indonesia are the two largest oil palm producing countries and is rich with numerous endemic, forest-dwelling species. Malaysia has tropical climate and is prosperous in natural resources. Currently, palm oil occupies the largest acreage of farmed land in Malaysia (Rupani et al., 2010).

2.2.1 Palm oil mill effluent (POME)

Palm oil milling is involved in the processing of oil palm fresh fruit bunches into crude palm oil and palm kernel. The by-products or wastes produced are in the forms of empty fruit bunches, mesocarp fibers, shells, palm oil mill effluent (POME) and boiler ash. The most voluminous and ecologically unfriendly is POME (Saifudin *et al.*, 2009). POME contains lots of fatty acid, which could yield a biodiesel through the transesterification. It is also contains substantial quantities of solids, which known as palm oil mill sludge (POMS).

Large quantities of water used during crude oil extraction process. From this quantity, 50% of the water results in the POME (Sethupathi S., 2004), while another 50% will be lost as a steam. POME is a high volume liquid wastes which are non-toxic, organic in nature but have an unpleasant odour and are highly polluting. It is non-toxic as there is no chemical were added during the oil extraction process. Fresh POME is hot and acidic with pH between 4 and 5. It is a brownish colloidal suspension containing high

concentration of organic matter. Khalid and Wan Mustafa, (1992) reported that POME is identified as a major source of an aquatic pollution by depleting dissolved oxygen when discharged untreated into the water bodies.



Figure 2.0: Palm Oil Mill Effluent (POME) pond, Kampung Endap, Samarahan.

2.2.2 Palm oil mill sludge (POMS)

POME consists of suspended solids and dissolved solids which left after the treatment. This solid also known as palm oil mill sludge (POMS). Therefore, due to large quantity of POME production every year, the amount of POMS increases respectively (Rupani *et al.*, 2010). POMS is a low grade oils from palm oil industry. The POMS usually contains high amount of free fatty acid high nutrient value than slurry. Besides, it can also lower the cost of biodiesel production which makes POMS a highly potential alternative feedstock for biodiesel production. The pH of sludge is 8.4 and it has bad odour. It is also considered as a source of surface and ground pollution. POMS is solid at ambient temperature.

Chooi (1984) reported that POMS can be dried and used as a fertilizer as it contain high nutrient value. The effectiveness was proved when it grows up the young oil palm seedlings. Higher nitrogen can be found in the high total solid POMS (Hashim et al., 1994).

2.3 Transesterification reaction

Transesterification, also called alcoholysis, is the reaction of an oil or fat with an alcohol to form esters and glycerol. Biodiesel is chemically defined as the monoalkyl esters of long-chain fatty acids derived from renewable biolipids. It is produced through the reaction of oil with alcohol in the presence of catalyst to yield methyl or ethyl esters (biodiesel) and glycerine (Demirbas, 2002). The type of alcohol used for transesterification is usually methanol (Chopade *et al.*, 2011). The conventional catalyst natural oil transesterification processes are selected among alkaline earth metal. Besides, transesterification could also be performed by using acid catalyst such as hydrochloric acid or sulphuric acid. However, the used of strong acid can cause a corrosion problem (Chouhan and Sarma, 2011).

The most common way to produce biodiesel is by transesterification of triglycerides of refined / edible types of oils using alcohol, in presence of an acid or a basic catalyst (Lopez *et al.*, 2005). In principle, although the transesterification is a reversible reaction, the back reaction does not occur or is negligible because the glycerol formed is not miscible with the biodiesel, leading to a two-phase system. Similar yields of biodiesel can be obtained using either metbanol or ethanol. However, the reaction time

is shorter in the methanolysis are due to the physical and chemical properties of methanol which are polar character and short chain of alcohol. For instance, Meneghetti *et al.* (2006) reported that the production of biodiesel from castor oil was faster with methanol compared to ethanol. Generally, methanol is preferred for transesterification because it is less expensive than ethanol (Graboski and McCormick, 1998).

2.4 Catalysts

Almost all production of biodiesel was using homogeneous catalysts (Romero *et al.*, 2010). However, the major disadvantage of homogeneous catalysts is the fact that these cannot be reused. The homogeneous process also implies further stages of washing, which involves an increase in production costs (Romero *et al.*, 2010). Due to the cost production of biodiesel, using heterogeneous catalysts was also reported to be carried out (Bourney *et al.*, 2005).

Heterogeneous catalyst is a very stable catalyst with no metal leaching. There is no formation either glycerate salts or metal soaps, which required no neutralization step and no introduction of water and there is no salt formation (Hillion *et al.*, 2003). MacLeod *et al.* (2008) reported that heterogeneous catalyst could improve the synthesis methods by eliminating the neutralization salts in the glycerol. Therefore, the number of separation steps can be reduced. Besides, heterogeneous catalyst exhibit less corrosive character and can be used in fixed-bed reactor, leading to safer, cheaper and more environment-friendly operation (Dossin *et al.*, 2006). It is can be operated at the similar

condition used for the homogeneous one or at the moderate temperature ($<250^{\circ}\text{C}$) and pressure ($<10\text{Pa}$).

In the previous research, the wastes from agricultural and food industries such as eggshells and mollusk shells has been reported to be used as a catalysts which afforded 94.1% of biodiesel. These shells contain alkaline earth metal which could be used, for example, MgO , CaO , SrO and BaO . However, the use of BaO is not practical enough since it is soluble in methanol and also forms highly toxic compound. The use of SrO is not preferable as catalysts. SrO possesses a strong tendency to react with carbon dioxide (CO_2) and water present in air to form strontium hydroxide and strontium carbonate, thus losing its catalytic ability (Yan *et al.*, 2008).

Among these catalysts, only MgO and CaO have the high activity for using in the typical process which at low temperature and under atmospheric pressure condition (Viriya-empikul *et al.*, 2011). Magnesium and zinc are actually acted according to homogeneous mechanism and end up as metals soap or metal glycerates (Hillion *et al.*, 2003). CaO was reported to have high basic strength and less environmental impacts due to its low solubility in methanol and can be synthesised from cheap sources like limestone and shells (Chouhan *et al.*, 2011). Besides, it has higher basicity, lower solubility, lower price and easier to handle than potassium hydroxide (KOH). Furthermore, CaO is nano-crystallized particle and it represented efficient characteristics as catalyst for transesterification reaction due to high surface area associated with the small crystalline sizes and defect.

Instead of using single metal oxides, CaO catalysts consisting NaOH supported with commercial silica were also prepared using impregnation method. The commercial silica was prepared from the natural resources. Some studies have reported the use of CaO or MgO supported on mesoporous silica, aluminas or zeolites, to provide greater surface area and therefore basicity (Di Serio *et al.*, 2006). Alkali and alkaline earth metals and their carbonates, hydroxides, halides and nitrates supported on alumina or silica have been examined as catalysts for transesterification (Endalew *et al.*, 2011). Mesoporous alumina and silica-supported (essentially calcium and potassium as active constituents) systems has been show to give nearly 100% yield in transesterification (Zhao, 2010).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

POME and POMS was obtained from cooling pond from Kampung Endap, Sarawak, Malaysia. It was heated to constant temperature prior to transesterification process. The analytical reagent grade methanol (Merck, Germany) was used in the transesterification reaction. Waste shells were obtained from the restaurant in the area of Samarahan and transformed to CaO catalysts by thermal synthesis.

3.2 Measurements

Glycerol and biodiesel were separated using Widespin Feedback Control Digital Timer Function. Infra-red (IR) spectra over the range $400\text{-}4000\text{cm}^{-1}$ were recorded on Perkin Elmer Thermoscientific Smart Omni Transmission Nicolet IS10 Fourier Transform Infrared Spectrometer (FTIR).